



Solvent Free Cationic Copolymerization of 2-Chloroethyl vinyl ether with Styrene, Catalyzed by Maghnite-H⁺, a Green Catalyst

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ABSTRACT

Maghnite-H⁺ (Mag-H), proton-exchanged Montmorillonite, catalyzed the cationic copolymerization of 2-Chloroethyl Vinyl Ether (CEVE) with Styrene (St) in a solvent free system. The objective is to synthesize an end-group functionalized copolymer. The advantage of the Mag-H lies in its capacity to solve ecological (green catalyst) and economic problems, and also to the fact that the reactions are carried out under moderate conditions, solvent free and at room temperature. A kinetic study was carried out, and the products obtained were characterized using different methods of analysis, including IR, ¹H and ¹³C NMR and viscosimetry.

Keywords: Vinyl Ethers, Copolymers, Green Catalyst, Maghnite-H⁺, 2-Chloroethyl Vinyl Ether.

INTRODUCTION

Polyvinyl ethers are viscous gum to rubbery solids used for a wide variety of technological and industrial applications; they are particularly employed in manufacturing additives and nanometer membranes. They are used in telecommunications, in the synthesis of nonlinear optical (NLO) materials¹, and also in electronics, in

the production of light emitting diodes (LEDs)². Chloroethyl Vinyl Ether (CEVE) is one of the most popular industrial products. CEVE is a special product because it possesses the functional group chloroethoxy that offers extremely varied possibilities for chemical modification and for anchoring functional groups. Hashimoto et al. employed CEVE as a starting material for preparing 2-vinylxyethyl phthalimide by substituting the



chlorine atom with potassium phthalimide. It was also used as a raw material in the synthesis of divinyl ethers^{3, 4}.

In recent years, both academic and industrial researchers have paid particular attention to green chemistry by developing organic and polymer syntheses that are respectful of the environment using renewable resources⁵. Solvent-free techniques, green solvents, water⁶, phase-transfer catalysts, or ionic liquids⁷ have replaced hazardous, toxic and volatile organic solvents⁸. On the other hand, enzymes⁹⁻¹⁵, silica gel and silica-supported reagents¹⁶, as well as clay minerals¹⁷⁻²⁵ are increasingly being used as catalysts. Furthermore, all reactions in this study are conducted at room temperature¹⁹⁻²⁵.

Herein, we propose to use smectite clay, called Maghnite-H⁺²⁰, as an efficient and recyclable green heterogeneous catalyst for the cationic copolymerization of Chloroethyl Vinyl Ether with Styrene at room temperature. The polymerization of vinyl ethers is widely known and has been used for a long time²⁶; this chemical reaction can only occur by a cationic mechanism. This is the case of Mag-H⁺ which can initiate the polymerization reactions only cationically¹⁹⁻²⁴. Moreover, Mag-H⁺ presents several advantages, among which are its high efficiency, easiness of handling, recyclability, high capacity to operate under mild conditions, and eco-friendliness.

MATERIALS AND METHODS

Materials

2-Chloroethyl Vinyl Ether (CEVE) was commercially supplied by (Sigma-Aldrich, 99%) and

used as received. Styrene (St) (Sigma-Aldrich, 99%) was washed with aqueous solution of NaOH (1N). Methylene chloride anhydrous (Sigma-Aldrich, ≥99.8%) and methanol (Sigma-Aldrich, 99%) were used as received. Raw-Maghnite was procured from Bental (Algerian Society of Bentonite).

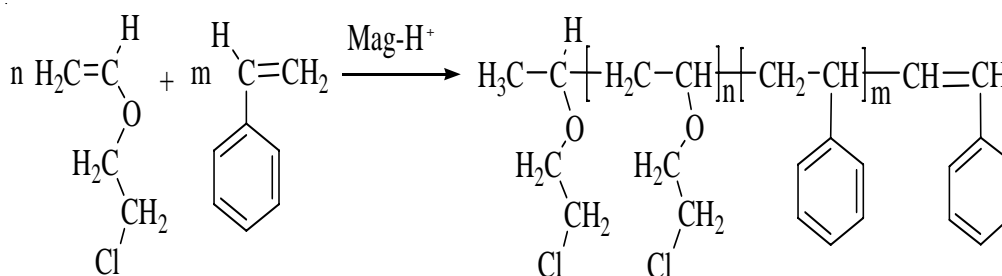
Methodology

Copolymerization of 2-Chloroethyl Vinyl Ether with Styrene using Maghnite-H⁺

Proton exchanged Montmorillonite clay called "Maghnite-H⁺" (Mag-H) is a non-toxic catalyst that was prepared according to the procedure reported in the literature^{19,20}.

Bulk copolymerization of CEVE with Styrene was carried out in a heterogeneous system, at room temperature, using a percentage, by weight relative to monomers, of Mag-H⁺ as a catalyst (scheme 1). Copolymerization was carried out with different mole fractions ($x = n_{\text{CEVE}}/n_{\text{ST}} + n_{\text{CEVE}}$), in several crimp tubes⁷. The mixture prepared was stirred with a magnetic stirrer for a specific period of time. Then, a given quantity of methylene chloride was added and the mix obtained was dried under vacuum in order to eliminate Mag-H⁺ which precipitates in methanol. Finally, the copolymer was isolated and dried before analysis. The experimental conditions used are described in Table 1.

In a previous study on CEVE and St polymerization, with Mag-H⁺ (3% by weight) as catalyst, reaches maximum yield after 6 hours of reaction^{22,24}.



Scheme 1. Copolymerization of CEVE with Styrene

Table 1: Experimental conditions for the copolymerization of CEVE with Styrene (St) catalyzed by Mag-H⁺ (1%) at room temperature. Time: 6h.

Mole fraction	n _{CEVE} (mmol)	n _{St} (mmol)	Yield (%)
0.2	4.70	18.78	31,88
0.3	4.70	10.95	36.29
0.4	9.39	14.09	54.78
0.5	9.39	9.39	57.45
0.6	9.39	6.24	63.15
0.7	18.78	8,07	69.38
0.8	18.78	4.70	71.50

Apparatus

In order to characterize our products, analytical techniques such as ¹H-NMR, ¹³C-NMR and IR were used. Viscosimetry was employed for the kinetic reactions.

¹H-NMR and ¹³C-NMR

The proton and carbon NMR spectra were recorded on a Bruker AC 300MHZ apparatus. This technique allowed identifying the products obtained. The analysis was carried out in deuterated chloroform.

Infrared IR

ATR-FTIR absorption spectra were

recorded on an Alpha Bruker ATR-FTIR spectrometer, in a range extending from 400 to 4000 cm⁻¹.

Viscosimetry

The intrinsic viscosity was measured at 25 °C, in methylene chloride, on an Ubbelohde capillary viscosimeter, Viscologic TI.1, version 3-1.

Characterization

Three mole fractions, 0.2, 0.5 and 0.8 were analyzed by ¹H NMR and one by ¹³CNMR spectroscopy. Fig. 1 and 2 show ¹H NMR spectrums and Fig. 3 shows ¹³C NMR spectrum.

Nuclear Magnetic Resonance (¹H-NMR) analysis

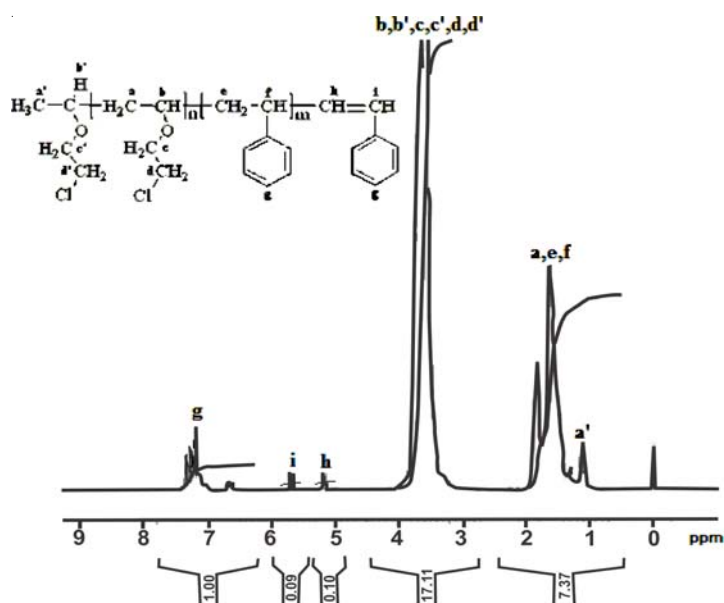


Fig.1. ¹H NMR spectrum of the CEVE-Styrene copolymer in DCCl₃ (300MHz). (x = 0.8)

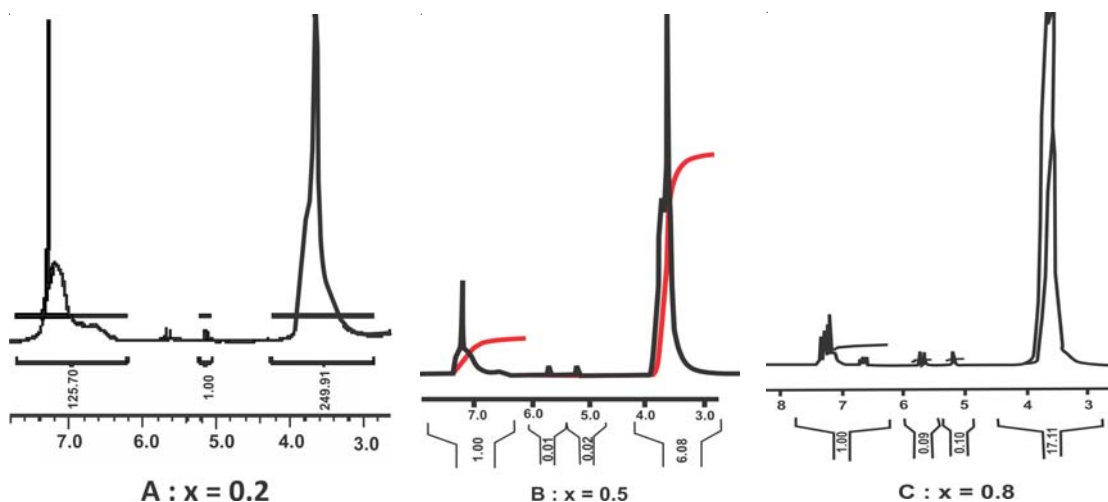


Fig. 2. ^1H NMR spectrum of the CEVE-Styrene copolymer in DCCl_3 (300MHz)

RESULTS AND DISCUSSION

The ^1H NMR analysis indicates the presence of the main protons corresponding to the (CEVE-Styrene) copolymer. The ^1H NMR spectrum of the copolymer is almost the same to that reported in the literature by Cramail²⁷. Peaks (i,h), observed between 5.2 and 5.80 ppm, correspond to H-vinyl of styrene of the chain end.

The number of CEVE and St units per chain in copolymer and M_n were determined by ^1H NMR (Fig. 2) from the ratio, on the one hand, between the $-\text{CH}_2-\text{CH}_2-\text{Cl}$ methylene protons, the $\text{CH}-\text{O}$ methine proton and aromatic proton of styrene and, on the

other hand, between the aromatic proton of styrene and H-vinyl of styrene of the chain end. Results are shown in Table 2.

Table 2: Number of CEVE and St units and \overline{M}_n values

X	m/n	N	m	\overline{M}_n
0.2	2	24	48	7611,12
0.5	6	9	54	6687,81
0.8	17	1	17	1914,48

Results show that in this copolymerization, CEVE is much more reactive than styrene. Values of $r_1 = 36$, $r_2 = 3$, and $66 \geq r_1 \geq 9$, $0.125 \geq r_2 \geq 0.01$ were reported respectively by Brown and Pepper²⁸ and Kanoh *et al.*,²⁹ for this system.

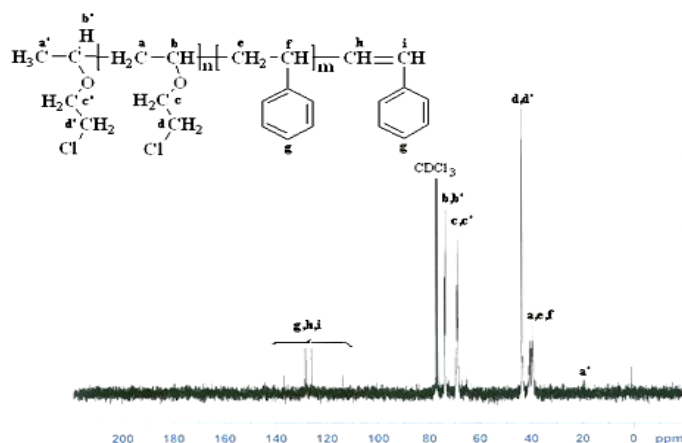


Fig. 3. ^{13}C NMR spectrum of the CEVE-Styrene copolymer in DCCl_3 (300MHz). ($x = 0.5$)

Nuclear Magnetic Resonance (^{13}C -NMR) analysis

Figure 3 shows ^{13}C NMR spectrum of the copolymer. The ^{13}C NMR spectrum shows the chemical shifts associated with the CEVE-St copolymer. Carbons of the CEVE unit resonate between 35 and 80 ppm. As for carbons of the aromatic ring, they resonate between 110 and

140 ppm. ^{13}C NMR Spectrum shows the difference between the reactivities of the two monomers by comparing the intensities of g and d peaks.

ATR-FTIR spectra

Figure 4 shows the ATR-FTIR spectrum of the copolymer (CEVE-Styrene)

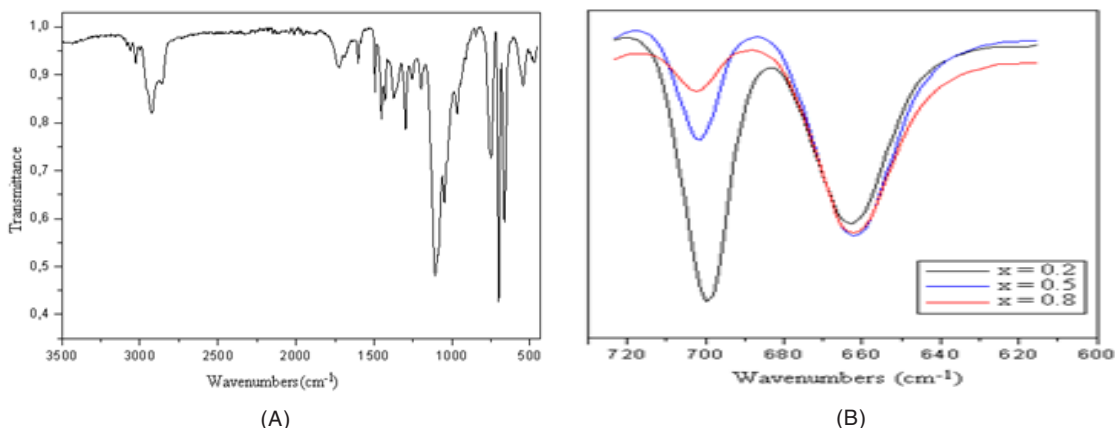


Fig. 4. ATR-FTIR spectrum of the copolymer (CEVE-Styrene). A: $x = 0.2$ and B: comparison between the intensities of absorption bands at 660 and 700 cm^{-1} .

Figure 4 shows the ATR-FTIR spectrum of the copolymer. The FTIR spectra indicate the presence of St and the CEVE units. As for the St repeating unit, aromatic C–H stretching occurs between 3000 and 3105 cm^{-1} , aromatic C=C stretching occurs at about 1600 cm^{-1} and St absorption of the out-of-plane ring deformation band occurs at about 700 cm^{-1} . Concerning the CEVE repeating unit, spectrum illustrates bands corresponding to C–Cl bond at about 660 cm^{-1} and C–O–C stretching of vinyl ether between 1090 and 1110 cm^{-1} . FTIR results from CEVE with St copolymerization showed that characteristic absorbance bands at about 700 cm^{-1} , the strongest IR band of St unit, and at 660 cm^{-1} , IR band of CEVE unit, could be used to follow the evolution of each unit in copolymer. Indeed, the comparison, between the intensities of absorption bands at 660 and

700 cm^{-1} , shows the great difference between the reactivities of St and CEVE (Fig. 4, B and Table 3).

Viscosimetric analysis

In order to understand the physical nature of the copolymers obtained, the evolution of their intrinsic viscosities was followed, in the solution of dichloromethane, at a temperature of 25 °C. The results obtained are grouped in Figure 6.

Kinetic study

The aim of the present study is to vary the amount of catalyst in order to examine its influence on the course of the living copolymerization.

Effect of the amount of Maghnite- H^+ on the yield

This study aims to know the behavior of our copolymer system, namely (2-Chloroethyl Vinyl Ether - Styrene) + Maghnite- H^+

Description of experiment

In order to determine the effect of the amount of the catalyst on the yield, three (03) series of experiments were conducted, by varying the percentages of the amount of Mag-H, as 1%, 2% and 3%. The results obtained are presented in Figure 5.

Table 3: Comparison between the intensities of absorption bands at 660 cm^{-1} and 700 cm^{-1}

X	$I_{\text{C-H (Aromatic)}}$	$I_{\text{C-Cl}}$	$I_{\text{C-Cl}}/I_{\text{C-H}}$
0.2	0.5615	0.3990	0.711
0.5	0.2450	0.4550	1.86
0.8	0.0867	0.4144	4.78

I: intensity of absorption bands

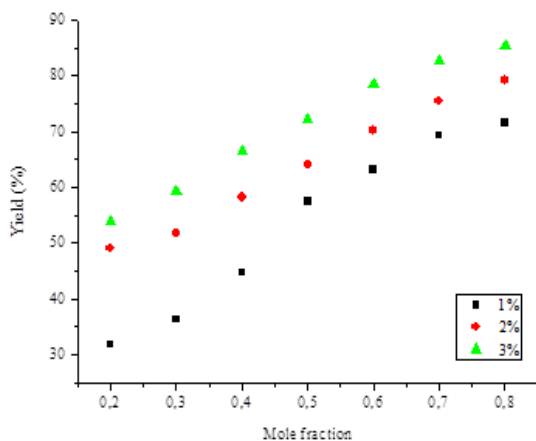


Fig. 5. Influence of the amount of Maghnite-H⁺ on the yield, during the copolymerization of the (CEVE -Styrene) system

Figure 5 shows the effect of the amount of Mag-H on the copolymerization rate of CEVE with Styrene. Indeed, using various amounts of Mag-H⁺, 1, 2, and 3 % by weight, the copolymerization was carried in bulk at room temperature. The copolymerization rate increased with the amount of Mag-H⁺, in which the effect of Mag-H⁺ as a cationic catalyst of the copolymerization is clearly shown. Similar results are obtained by Beloufa *et al.*,³⁰ and Bouchama *et al.*,³¹ in, respectively, the copolymerization of 1,3,5-trioxane with 1,3-dioxolane and ϵ -caprolactone with tetrahydrofuran catalyzed by Mag-H⁺. This increase in yield is due to an increase in the number of "initiating active sites" responsible of inducing polymerization, a number that is proportional to the amount of catalyst.

Effect of the amount of Maghnite-H⁺ on intrinsic viscosity

The different samples obtained from the different experiments were subjected to the viscosimetric analysis. The results are shown in Fig. 6. As is shown, on the one hand, the increase of the catalyst amount led to the decrease of intrinsic viscosity. This is comparable to that of the most active catalyst systems. The explanation for the decreased of intrinsic viscosity is that the chain transfer reaction rate is faster than that of the propagation reaction. On the other hand, the decrease in the quantity led to the increase of the intrinsic viscosity, this is due

to the high reactivity of CEVE which leads to the formation of oligomers²². From the results obtained, it can be said that the intrinsic viscosity decreases as the amount of Maghnite-H⁺ goes up. Moreover, the intrinsic viscosity increases with increasing percentage (%) of the most reactive comonomer. In this case, styrene ($r_1 = 160$) is more reactive than CEVE ($r_2 = 0.07$), and this difference in reactivity between the two monomers is due to the fact that the two types of active centers react with the most reactive monomer. The reaction mixture is therefore enriched with styrene, which is more reactive than CEVE. This causes the yield to decrease, while the intrinsic viscosity increases.

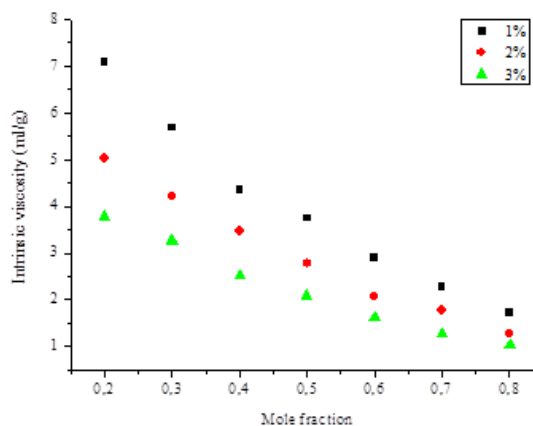
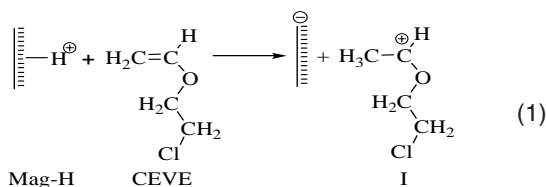
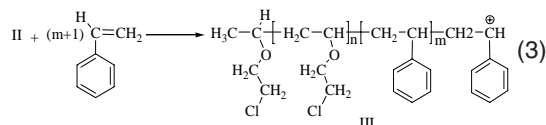
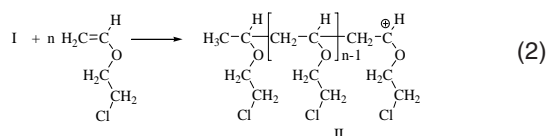


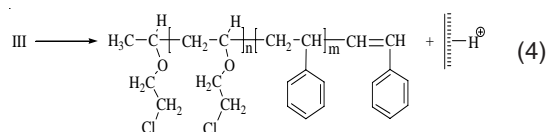
Fig. 6. Influence of the amount of Maghnite-H⁺ on the viscosity $[\eta]$ during the copolymerization of the system (CEVE -Styrene)

Proposed mechanism

The copolymerization is proposed undertaking in a way as shown in Scheme 2. Mag-H performs as an environmentally friendly solid catalyst. It was regarded as an initiator and activator^{19-24, 31}. The copolymerization of CEVE with St is initiated, firstly, by proton addition from Mag-H to CEVE (Eq. 1), due to the most reactivity of CEVE compared to the St, and the Maghnite takes place as counter-ion. Propagation then takes place by conventional cationic mechanism (Eq. 2). Secondly, reaction between growing macrocation and St occurs (Eq. 3). The copolymerization ends by proton transfer to St and/or to Maghnite produced by unsaturation as shown in the termination reaction (Eq. 4).

Initiation**Propagation****Termination**

We suppose that there was formation of a double bond at the end of the chain of the copolymer by spontaneous transfer.

**CONCLUSION**

The main goal was the synthesis of copolymers using an environmentally friendly solid catalyst. Our study aimed particularly at

investigating the copolymerization of vinyl monomers, such as 2-Chloroethyl Vinyl Ether (CEVE) and Styrene (St). The cationic bulk polymerization, catalyzed by Mag-H⁺, occurs telechelic copolymer which is characterized by various methods, like ¹H-NMR, ¹³C-NMR, FTIR, and Viscosimetry. ¹H-NMR, ¹³C-NMR confirmed the production of poly (CEVE-co-Styrene) with styrenic unsaturation end chain which gives a monotelechelic copolymer.

The kinetic study of cationic copolymerization in the presence of Mag-H⁺ makes it possible to draw the following conclusions

- bulk copolymerization is possible,
- yield increases with increasing amount of Mag-H⁺,
- yield decreases with increasing percentage of the most reactive comonomer,
- increasing the amount of Mag-H⁺ leads to a decrease in the intrinsic viscosity,
- intrinsic viscosity increases while increasing the percentage of the most reactive comonomer.

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